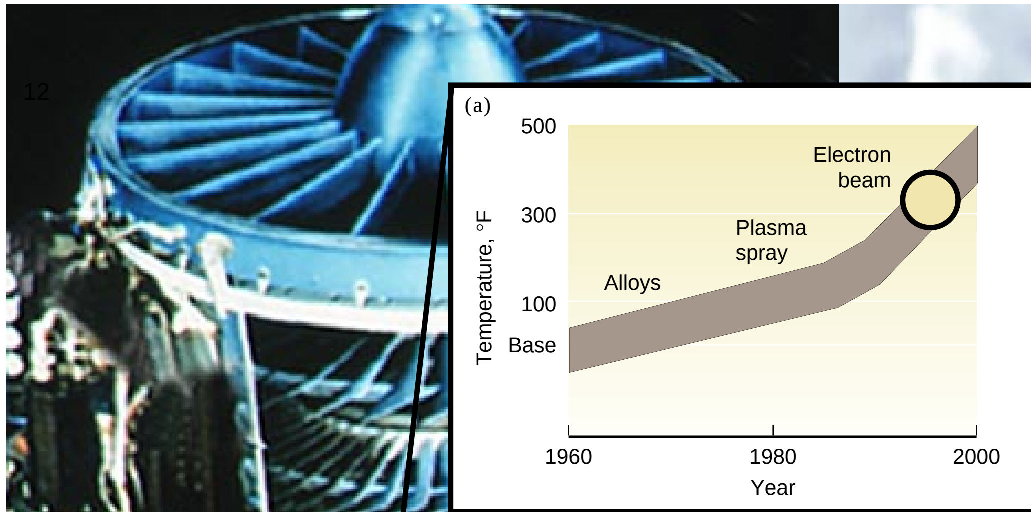
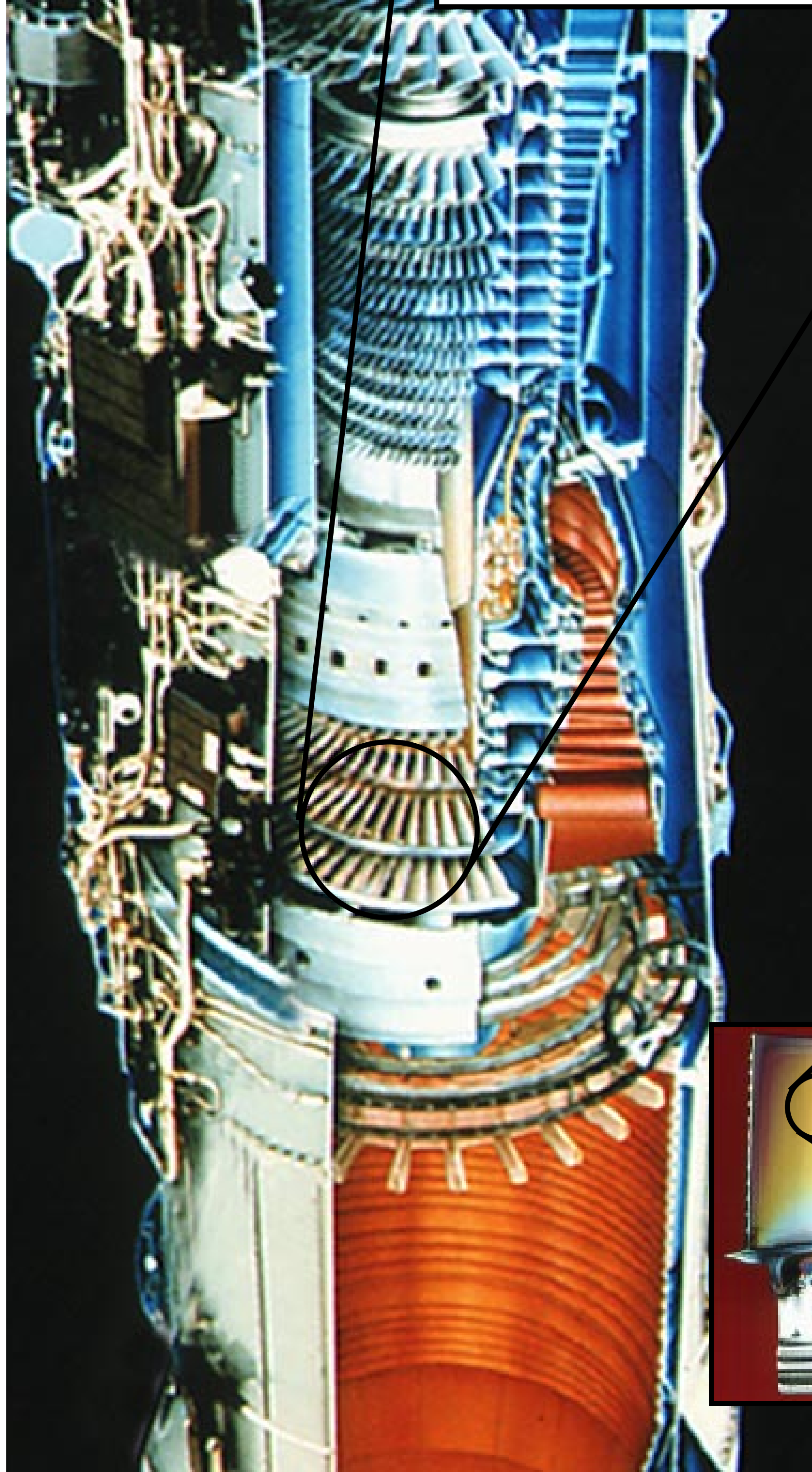
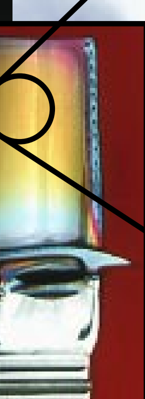
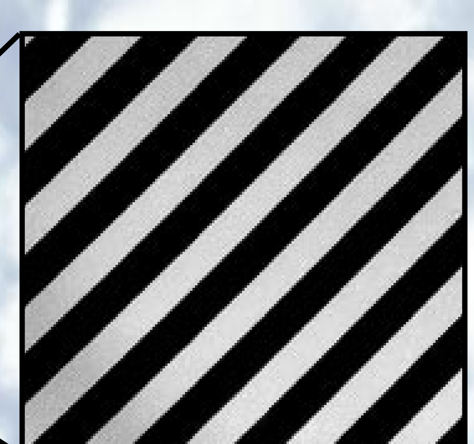


Figure 1. (a) Multilayer materials in aircraft engines withstand greater temperatures, which allow engines to develop greater thrust. (b) A turbine's airfoil thermal barrier coating prolongs engine lifetime.

(b)







Atomic Engineering with Multilayers

The future looks bright for multilayers, exceedingly thin alternating layers of materials that often demonstrate remarkable—and unpredictable—properties for a host of applications.

A common adage goes, "thin is beautiful." To a growing number of researchers—and intrigued companies—the saying is especially true for a unique class of materials called multilayers. Composed of alternating layers of two different materials as thin as a few atoms, multilayers offer extraordinary strength, hardness, heat-resistance, and unexpected new properties. At Lawrence Livermore National Laboratory, researchers are pioneering entirely new applications for these materials, which many now believe to constitute an essentially new state of matter.

Multilayers' alternating layers can vary in number from a few to more than 200,000. Individual layer thicknesses range from a few atoms to a few thousand atoms, corresponding to a maximum structure thickness of about 10 millionths of an inch. The repeat distances in the multilayers, that is, the thickness of two adjacent layers, can be purposely selected to be identical to the interaction lengths characteristic of important physical properties (e.g., magnetic interaction lengths) to yield new properties. In this context, says Laboratory material scientist Troy Barbee, Jr., one of the pioneers of modern multilayer technology, "it is generally accepted that one should expect the unexpected when multilayers are fabricated and experimentally characterized."

Multilayers are part of a larger, established scientific field of so-called designer or "nanostructured" (from nanometer, a billionth of a meter) materials that represent the current limits of materials engineering and that are currently impacting numerous Laboratory research programs. Indeed, multilayers are among the first materials to be designed and fabricated at the atomic level, a capacity termed "atomic engineering" by Barbee. "We're building multilayer materials atom by atom and molecule by molecule," he says. The result is tremendous potential for improving the performance of large numbers of products through either new or enhanced mechanical, optical, magnetic, thermal, and other physical properties.

To date, Barbee's team of material scientists, engineers, and technicians has synthesized multilayers from 75 of the 92 naturally occurring elements in elemental form or as alloys or compounds. With that wealth of experience, the team has emerged as one of the world leaders in multilayer science and its applications. The team has also forged partnerships with other national laboratories, U.S. industries, universities, federal agencies such as the Department of Defense and NASA, and researchers worldwide.

The first applications of multilayer structures were demonstrated more than 50 years ago for such uses as optical interference filters and reflection coatings. During the 1970s, "macro" multilayer films became essential to the semiconductor industry for making everything from computer chips to hard disk drives. In the late 1970s, Barbee pioneered significant advances in fabrication technology in the development of multilayers for a wide variety of applications in the x-ray, soft (lower energy) x-ray, and extreme ultraviolet (EUV) regions of the electromagnetic spectrum. For example, high-reflectivity multilayer mirrors have made possible a new class of telescopes for solar physics and astronomical research. Multilayer optics also have found applications in electron microprobes, scanning electron microscopes, x-ray lasers (especially in laser-fusion diagnostic systems), and particle beamlines in accelerators.

To Save Airlines Millions

Livermore researchers are currently pioneering new kinds of multilayers—beyond optical uses—that take advantage of their extraordinary properties. These applications include high-performance capacitors, ultrahigh-strength materials, thermo-electric devices, and coatings for gears and bearings, aircraft and automobile engines, and cutting and machine tools.

Products incorporating multilayers promise higher strength-to-weight ratios, less friction and wear, higher temperature operation, corrosion resistance, fracture toughness, and low electrical resistivity. Multilayer technologies can also have a profound impact on manufacturing processes by decreasing the amount of

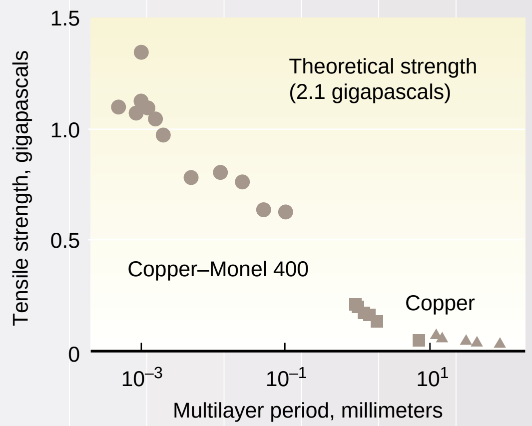


Figure 2. Strength tests show the difference between commercial copper and the copper–Monel multilayer material.

machining necessary between raw material and finished product.

The enormous commercial potential of multilayers has not gone unnoticed by U.S. industry. A recently completed three-year Cooperative Research and Development Agreement (CRADA) joined scientists from Lawrence Livermore, Pratt & Whitney, and Rohr Inc. to develop high-performance multilayer coatings for aircraft engine blades and high-strength engine parts (Figure 1). Such advances could safely increase the operating temperatures of gas turbine engines by 10 to 38°C, thereby permitting the engines to develop greater thrust. The coatings would also prolong the life of many parts throughout the engine, conceivably saving commercial airlines and the Department of Defense tens of millions of dollars annually.

Such coatings work because extremely thin slices of matter exhibit new and sometimes unanticipated properties. Scientists believe the reason is their extensive "boundary structure." In a multilayer with layers only four atoms thick, half of the atoms lie at an interface between the layers. They do not develop the conventional molecular structure and bonding found in pieces of matter greater than 100 nanometers in diameter. As a result, the layers are stronger and less likely to fail under stress. Multilayers made of metals get stronger and harder, while multilayer ceramics become less brittle. The strongest materials are those with the thinnest layers because they have the most uniform structure.

Barbee says it is a complex task to choose materials to make up a multilayer because a researcher must understand metallurgy as well as the physics of the intended application. Indeed, combinations of two materials sometimes result in surprising new properties. A multilayer fabricated by Livermore scientists and composed of copper and Monel (copper–nickel alloy) (Figure 2) has more than 10 times the strength of copper alone and is highly resistant to chemical corrosion. Sometimes materials with different properties can be combined in multilayers to eliminate or mitigate some of their individual drawbacks. For instance, very hard materials can be combined with those that are very tough to produce something, such as copper–Monel, that is both hard and resistant to cracking.

One multilayer designed by Barbee illustrates the advantages gained by adding even a small quantity of a different material. This multilayer is composed of 7,100 individual layers of materials—3,550 layers of copper (each layer is 325 angstroms, or 156 atoms, thick) and 3,550 layers of a copper–zirconium mix (each layer is 100 angstroms, or 38 atoms, thick). All told, the multilayer measures about 142 micrometers thick, equivalent to the thickness of about two human hairs. Although only about three atoms in every hundred are zirconium, the material has a tensile strength of about a billion pascals (160,000 pounds) per square inch, more than six times the strength of commercial copper. With their high strength, nonmagnetic nature, and more environmentally friendly materials, copper–zirconium multilayers could be used to replace beryllium– copper alloys commonly used in springs and tools.

Seeing the Sun in New Ways

One of the most important applications of multilayers is astronomical imaging. High-performance multilayers have been used as mirrors to focus light in the x-ray, soft x-ray, and EUV regions. Images taken by telescopes using multilayer mirrors reveal important features that cannot be captured by standard imaging instruments operating at longer wavelengths. Furthermore, because multilayer mirror surfaces are reflective only within a certain wavelength range, they can be used to isolate a particular region of the spectrum of interest to astronomers (Figure 3).

Barbee notes that standard optical techniques cannot be used in x-ray imaging devices because x rays are substantially absorbed by the materials. As a result, reflective optics based on collective scattering of the individual layers in a multilayer solid are used to collect and image the x rays. X rays are reflected only if they hit a metal surface at a very shallow, or grazing, angle. However, natural crystals have spacing between their planes on the order of a few angstroms, which limits the

reflection angles and x-ray wavelengths for which they can be used. To retain this range of reflected light, one can use a series of multilayers to replace the natural crystals. An added advantage of multilayers is that they can be smoothly deposited on curved substrates, a requirement for high-performance optical systems.

Barbee's work on multilayer optics began in the 1970s at Stanford University, where he was laboratory director of the Center for Materials Research. He led development of multilayers using a technique called magnetron sputter deposition, now the most common technique for depositing multilayers on substrates (see box, p. 18). In 1976, the technique was reported to Congress by the National Science Foundation as a major breakthrough in material science.

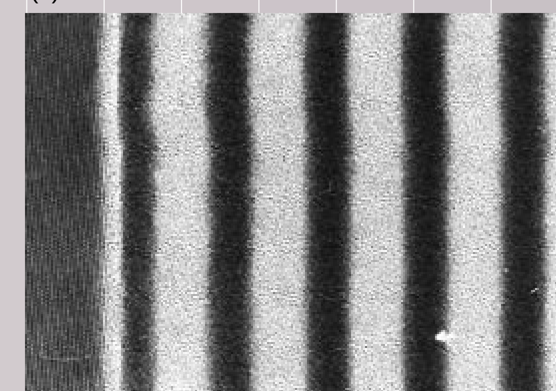
Barbee and his staff at Stanford designed a set of magnetron sputtering sources to produce multilayers based on copper layered with the transition metals niobium, tantalum, molybdenum, and tungsten. From analyzing these early multilayers, they found that the structures might be of x-ray optical quality.

An effort was begun to explore this opportunity with the material pair tungsten and carbon. These elements were selected because only a minimum number of layers were required to achieve significant reflectivity, minimizing the demands on the stability of the maturing sputtering process. These materials proved to be very effective and have been a staple of the international multilayer x-ray optics field ever since. In addition, the development effort was aided by the appearance of new tools, namely the scanning transmission electron microscope (STEM) for characterizing multilayer structures and synchrotron x rays for characterizing mirror performance.

When Barbee came to Livermore in 1985, he set out to advance the sputtering process, develop more advanced multilayer optics, and explore a wider range of multilayer applications. Today, Livermore is known internationally for the design and manufacture of optics for obtaining high-resolution images of the Sun and astronomical objects in the x-ray to EUV spectrum. The Livermore team made the multilayer optics for a Cassegrain telescope on the Stanford University/Marshall Space Flight Center sounding rocket launched on October 23, 1987. The images (Figure 4) clearly resolved features, such as loops and plumes, of the Sun's corona for the first time in this region of the electromagnetic spectrum. One of the photos appeared on the September 20, 1988, cover of *Science* magazine.

Since then, Livermore researchers have manufactured multilayer optics used in several satellites by the U.S., the U.K, and France. Livermore multilayer optics for an x-ray telescope will be onboard a new NASA research

(a)



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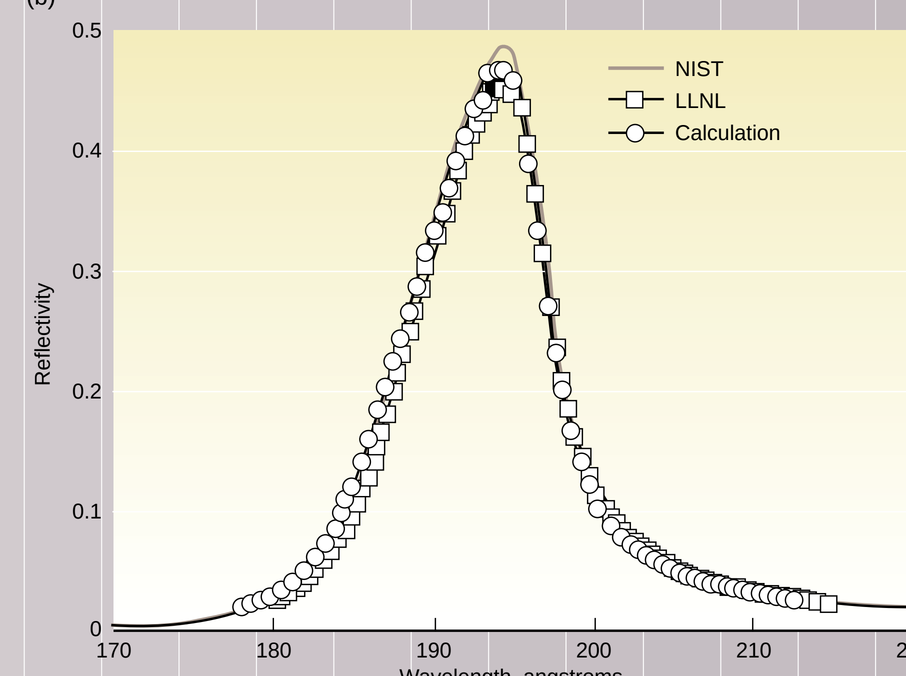


Figure 3. (a) Multilayers of molybdenum carbide and amorphous silicon (Mo_2C/Si) are shown in a transmission electron microscopy image at 4 million magnification after annealing at 500°C. (b) Reflectivity measurements of Mo_2C/Si, taken by Lawrence Livermore and the National Institute of Standards and Technology (NIST), are extremely close to the theoretical calculation of a perfect structure at the wavelengths shown.

Figure 4. Early advances in multilayer technologies brought images of the Sun with higher resolution than previous grazing incidence telescope images. The reason: multilayer laminates in the x-ray optics allow the use of a normal incidence optics system for which aberrations can be minimized.

satellite scheduled to be launched by a Pegasus spacecraft in December 1997. The x-ray telescope is designed to have the highest spatial resolution of any such instrument ever flown. Livermore multilayer optics are also being considered for two other U.S. space missions and for satellites for the Japanese and European space programs. The popularity of the multilayer optics is a significant factor in the growing interest in x-ray imaging of astrophysical phenomena from stellar sources.

The outstanding properties of Livermore's x-ray optics can be seen in STEM images of multilayers containing alternating layers of molybdenum carbide (Mo_2C) and amorphous silicon (Si). The image (Figure 3a) shows that the interfaces between the multilayers are very smooth and abrupt in contrast, with no intermediate chemical reaction layer at the interfaces of the two layers. Figure 3b shows that the measured reflectivity of the multilayer is essentially equal to that predicted for a perfect structure.

Extensive Effort Under Way

The Laboratory-wide multilayer development effort consists of more than 15 senior researchers and 25 technicians at work in five laboratories. The results of their work can be seen across Lawrence Livermore's directorates—Chemistry and Materials Science, Engineering, Defense and Nuclear Technologies—and especially in the Laboratory's Laser Programs. Barbee's team produced more than 250 multilayer optics last year for laser applications, particularly for laser-fusion research.

"Using multilayer technology, we've been imaging high-energy-density plasma of the Sun and then turning around and imaging the same kinds of phenomena in laser fusion," Barbee explains.

Multilayer optics make possible x-ray interferometry for characterizing plasmas created by high-power lasers. The technique provides the only workable diagnostic tool to directly look at extremely hot, high-electron-density plasmas of matter produced in inertial confinement fusion experiments (Figure 5).

Researchers in Lasers' Advanced X-Ray Optics Group are using multilayer mirrors in recently developed soft x-ray lasers. One potential use of a laboratory x-ray laser is in imaging biological samples. A spherical multilayer mirror is used to condense x-ray laser light onto living organisms to obtain a high- resolution (greater than 800 angstroms) image.

Barbee's team is also collaborating with researchers in Lasers' Advanced Microtechnology Program to make possible computer chips with 10 times the performance yet one-tenth the size of today's devices. Achieving these breakthroughs will be possible only with lithography using EUV light. The new EUV technology is the focus of a major CRADA announced in September 1997 by Department of Energy Secretary Federico Peña. As with today's deep-ultraviolet-light-based technology, EUV lithography will employ multilayers in creating computer chips and their master patterns, called masks.

Capacitors around a Corner

One research avenue of significant potential is using multilayers as ultra-compact, high-energy storage, and extremely cost-effective capacitors made up of alternating metal (conductor) interdigitized with dielectric (insulator) layers. Power electronic "snubber" capacitors, normally made of ceramic or polymer dielectrics, and similar in size to a C battery, are usually connected to much smaller solid-state switching devices. These capacitors typically store 0.1 to 0.2 joules per cubic centimeter capacitor volume and are widely considered the limiting factor in many applications. In contrast, multilayer capacitors the size of a postage stamp would store 10 joules per cubic

centimeter while costing perhaps one-twentieth that of their ceramic forebears.

Project leader Gary Johnson, an electronics engineer, says that the first commercial multilayer capacitors will likely be targeted at power electronics, computers, and communication devices. Compact multilayer capacitors, for example, would be highly useful in power conditioners that convert dc to ac (or vice versa) and for adjustable-speed motor drives.

Johnson says longer-term multilayer capacitor applications include temporary energy storage for physics experiments such as high-energy lasers. Other potential applications include electric motor controls and energy ballasts for batteries in electric vehicles. Multilayer capacitors could deliver at least 100 times more power per unit of volume than anything available today for electric vehicles. Multilayer capacitors have the potential to be especially useful in regenerative braking, in which the considerable energy dissipated in braking is converted by a generator back into electricity to recharge capacitors (see *S&TR*, October 1995, p. 12). Realizing the potential of these large storage applications, however, is dependent upon substantial advances in multilayer capacitor fabrication processing, the next major research and development thrust of this work.

The present multilayer capacitor effort focuses on honing the manufacturing process, in particular, eliminating sources of contamination. When a layer is only a few atoms thick, even the tiniest dust particle can severely compromise capacitor performance, Johnson notes. The Livermore team is in early discussions with capacitor manufacturers and tooling companies to license this technology. Johnson says capacitor companies are particularly enthusiastic about the high energy density offered by multilayer capacitors because they could create entirely new markets.

Another application that may soon see commercial use is a multilayer foil made of reactive materials such as aluminum and nickel that would act as a highly portable welding tool. A piece of the multilayer could be slipped into a break or crack of metal, for example, and the foil would be lit with a match. The multilayer would quickly reach a temperature of up to 2,000°C to repair the crack. The multilayer materials would be chosen to produce different temperatures and rates of heat release to correspond to the material being welded.

Replacing Loud Compressor

Further away from commercial realization than multilayer capacitors or welding materials, yet with as many potential applications, are multilayer thermo-electrics. The thermo-electric effect uses heat transported by electrons to produce cooling with electrical current. Conversely, thermo-electric materials can also take advantage of diffusion of electrons in a thermal gradient to produce a current. Thermo-electric materials have no moving parts, so they can be miniaturized and may be very reliable. Current applications include temperature-sensing thermocouples, electric power generators for spacecraft, and portable food and beverage coolers.

The application of thermo-electric devices for cooling or heating large equipment is primarily limited by their efficiency, which is lower than that of conventional gas cycle refrigeration. However, the development of multilayers has sparked interest that multilayer thermo-electric materials may be the key to taking these devices into the commercial mainstream.

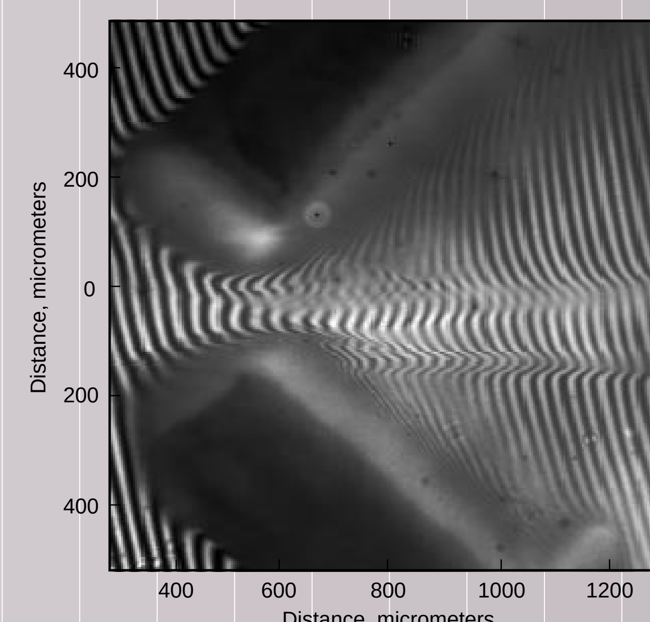
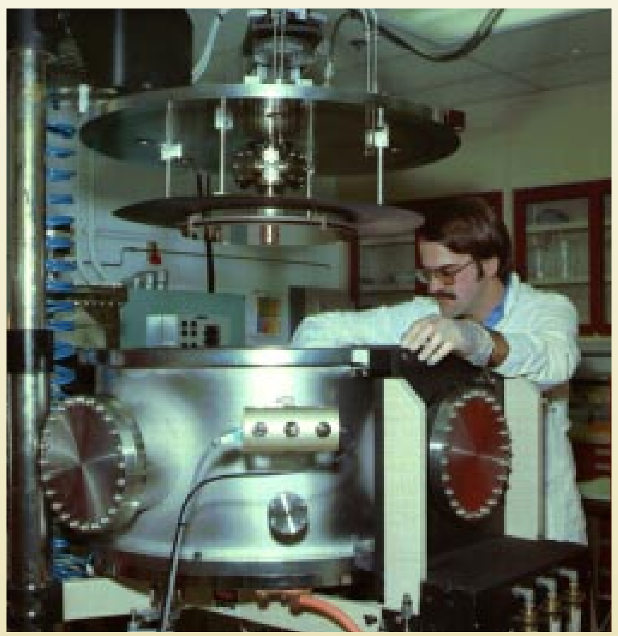


Figure 5. Where no other systems have worked, multilayered optics allow an x-ray interferometry measurement of electron-density, colliding-plasma experiments relevant to inertial confinement fusion.

Making Multilayers by Sputtering

In manufacturing multilayer materials, the Livermore team uses a process called sputtering, a technique created more than a century ago. Livermore materials scientist Troy W. Barbee, Jr., applied an advanced form of sputtering, called magnetron sputtering, to fabricating multilayers in the 1970s. Today, the semiconductor industry, for example, uses magnetron sputtering to deposit thin films on computer parts, and the machine tool industry uses the technique to apply hard coatings to cutting tools. It is even used to tint windows by forming thin, optically active interference coatings of metal upon glass and to coat jewelry with gold-appearing coatings.



Dan Noecker of Livermore's vapor-phase deposition laboratory adjusts atom-by-atom fabrication of a new class of materials for high-strength and high-temperature applications.

Most of the sputtering work at Livermore takes place at the vapor-phase deposition laboratory. Here, technicians secure a substrate to a table that rotates over two magnetron sputter sources of material for the multilayer. The table rotates at a predetermined speed, and the alternating layers are quickly built up as the substrate passes over first one material source and then the other. The sputter sources operate by bombarding plates of the material to be deposited with high-energy argon gas ions. The impact of these ions blasts atoms from the surface of the sources into the vapor and onto the substrate. As the multilayers revolve from magnetron source to magnetron source, the alternating layers, ranging from a few to many thousand, are sequentially formed.

Sputtering gives a constant deposition rate in which the thickness of each layer is precisely determined by the distance of the substrate from the sources and the time the substrate spends over each source. The technique enables layer thickness control of one-hundredth of an atomic diameter for up to one thousand layers. This process can also achieve a layer thickness uniformity of better than 0.7% (approximately one-thirtieth of an atomic diameter) over a 10-centimeter-diameter substrate (see photo at left).

To help evaluate the performance of multilayers, researchers use a soft x-ray diffractometer that was designed and built at Livermore. It is contained in a vacuum chamber and scans the surface of a sample under computer control to provide a map of reflectivity uniformity. In addition, samples are sectioned and thinned for electron microscope analysis to inspect interface sharpness, layer-to-layer uniformity, and layer smoothness.

"Multilayers may have the potential to increase the efficiency of thermo-electric materials by a factor of three or four," says Livermore material scientist Andrew Wagner. He notes that an efficient multilayer thermo-electric cooling system could replace the conventional large, heavy, and noisy refrigerator compressor that often cycles on and off. A multilayer thermo-electric device would be silent, operate continually, and not require environmentally unacceptable hydrofluorocarbon gases.

Wagner, together with researcher Joseph Farmer and technicians Ronald Foreman and Leslie Summers, has conducted basic research on the feasibility of producing multilayer thermo-electric materials, which, in that application, would require millions of alternating layers of conducting and insulating materials.

Another area of active development is using multilayers as optics for imaging sources of neutrons. This application has important implications for the Department of Energy's Stockpile Stewardship and Management Program because high-energy neutron radiography can be used to image low-density materials for surveillance of stockpile nuclear assemblies. For physics research applications, the Livermore team is collaborating with the University of Illinois on a new neutron beamline that makes use of multilayers as optics for neutrons from a variety of sources.

The neutron work is another application for multilayers. But multilayers have that way about them: they force new thoughts about making materials—this time on the atomic scale—and finding applications that will benefit society.

—Arnie Heller

Key Words: multilayers, nanostructured materials, sputtering, thermo-electrics, x-ray optics, x-ray lasers.

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About the Scientist

TROY W. BARBEE, JR., is a materials scientist at the Laboratory, focusing on the science, technology, and application of multilayers. Before arriving at Livermore in 1985, Barbee was at Stanford University, where he was a senior research associate in the Department of Materials Science and Engineering and laboratory director at the Center for Materials Research. Barbee also was a visiting professor in San Jose State University's Materials Science Department and at the Stanford Research Institute. Barbee received his B.S. in metallurgical engineering and his M.S. and Ph.D. in materials science engineering from Stanford.